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(54) **Cleaning composition and method for using the same**

(57) A dry cleaning composition utilizes a stain removal surfactant and a stain removal solvent chosen from a solvent which is a gas at standard temperature and pressure, a biodegradable functionalized hydrocarbon, or a silicone solvent.

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(a) at least one solvent selected from the group consisting of a solvent that is a gas at standard temperature and pressure, a biodegradable functionalized hydrocarbon or a silicone comprising solvent;

(b) optionally, a polar fluid;

(c) a substrate treated with a stain removal composition comprising at least one stain removal surfactant, the stain removal surfactant being a nonionic, anionic, cationic, amphoteric or zwitterionic compound or mixture thereof; and

(d) optionally, a continuous phase surfactant, the continuous phase surfactant capable of forming a reverse micelle in a continuous phase formed by the solvent.

[0012] In a fourth embodiment, the present invention is directed to a process of dry cleaning in a solvent, which is a gas at standard temperature and pressure, a biodegradable functionalized hydrocarbon or a silicone comprising solvent, using the stain removing composition described above.

[0013] In a fifth embodiment, the present invention is directed to a substrate having been subjected to the dry cleaning process of this invention.

Detailed Description of the Preferred Embodiments

[0014] There generally is no limitation with respect to the solvent (i.e., fluid) employed in this invention other than that the solvent is a gas at standard temperature and pressure, a biodegradable hydrocarbon or a silicone comprising solvent, and capable of being a continuous phase in a dry cleaning application. Illustrative examples of the types of solvents which may be employed in this invention include a C₂-C₄ substituted or unsubstituted alkane, carbon dioxide, silicone oil, and an azeotropic solvent.

[0015] Regarding the solvent which is a gas at standard temperature and pressure, such a solvent may be, within the dry cleaning composition or process, a gas, liquid or supercritical fluid depending upon how densified the solvent is (how much pressure is applied at a given temperature) in the domestic or commercial cleaning application the solvent is used in. Propane and carbon dioxide tend to be the preferred solvents when the solvent selected is one which is a gas at standard temperature and pressure. Carbon dioxide, however, is especially preferred.

[0016] As to the silicone comprising solvent which may be used in this invention, such a solvent is typically a commercially available cyclic-siloxane based solvent made available from GreenEarth Cleaning, LLC. Such a solvent is generally one which has a flash point over about 65°C, with octamethylcyclotetrasiloxane and decomethylcyclopentasiloxane being most preferred. A more detailed description of such conventional siloxane comprising solvents may be found in U.S. Patent No. 5,942,007, the disclosure of which is incorporated herein by reference.

[0017] The biodegradable functionalized hydrocarbon that may be used in this invention includes those generally classified as an azeotropic solvent. Such an azeotropic solvent often comprises alkylene glycol alkyl ethers, like propylene glycol tertiary-butyl ether, and is described in United States Patent No. 5,888,250, the disclosure of which is incorporated herein by reference. Moreover, as used herein, biodegradable functionalized hydrocarbon is defined to mean a biodegradable hydrocarbon comprising at least one member selected from the group consisting of an aldehyde, ketone, alcohol, alkoxy, ester, ether, amine, amide and sulfur comprising group.

[0018] Regarding the stain removal composition of this invention, such a composition comprises a stain removal surfactant that may generally be classified as a nonionic, anionic, cationic, amphoteric or zwitterionic compound. The stain removal surfactant which may be used in the stain removal composition of this invention is limited only to the extent that it minimizes the impact of the forces and interactions between the contaminant targeted for removal and the substrate. In addition to minimizing such forces and interactions, it is preferred that the surfactant employed in the stain removal composition is one that increases the solubility of the contaminant in the stain removal solvent being used, or suspends the contaminant in the stain removal solvent by forming lamellar micelles, or both.

[0019] Illustrative examples of the nonionic surfactants which may be used in this invention include fatty alcohol polyalkylene ethers resulting from condensation reactions, like fatty alcohol polyethylene glycol ethers and polyethylene/polypropylene (copolymer) glycol ethers. Such surfactants typically have an aliphatic portion comprising from about 8 to about 18 carbon atoms and about 2 to about 65 moles of alkoxyated portion per mole of aliphatic group. As to the alkoxyated portions, they are typically about 1:10 to about 10:1 ethylene oxide:propylene oxide when copolymers are employed. Other nonionic surfactants include ethylene oxide-propylene oxide block copolymers (weight average molecular weight of about 500 or more with ethylene oxide:propylene oxide portions being in a ratio of about 1:10 to about 10:1) and (C₈-C₁₈) fatty acid (C₁-C₈) alkanol amides like fatty acid ethanol amides.

[0020] Additional nonionic surfactants which may be used in the stain removal composition of this invention include N-alkylpyrrolidones, like N-octylpyrrolidone; polyalkylene oxide condensates of alkylphenols whereby the alkyl group has from about 5 to about 15 carbon atoms (straight or branched), the alkylene oxide preferably being ethylene oxide with from about 2 to about 65 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent is limited only to the extent that it does not interfere with the formation of the compound. Such a substituent is often derived from a C₆-C₁₄ alkane.

commercial preparations at levels sufficient to provide from 0.0005 to 0.2 Anson units (AU) of activity per gram of stain removal composition.

[0033] Non-limiting examples of suitable, commercially available, proteases that may be used include pepsin, trypsin, ficin, bromelin, papain, rennin, and mixtures thereof. Other suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Another suitable protease is obtained from a strain of *bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE®. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784. Still other enzymes include Protease A (European Patent Application 130,756, published January 9, 1985); Protease B (European patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bot et al., published January 9, 1985); and proteases made by Genencor International, Inc., according to one or more of the following patents: Caldwell et al., U.S. Patent Nos. 5,185,258, 5,204,015 and 5,244,791, all of which are incorporated herein by reference. Other enzymes suitable for removing protein-based stains that are commercially available include those sold under the trade names ALCALASE® and SAVINASE® by Novo Industries A/S (Denmark) and MAXATASE® by International Bio-synthetics, Inc. (The Netherlands).

[0034] A wide range of enzyme materials and means for their incorporation into compositions are also disclosed in U.S. Patent No. 3,553,139, issued January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent No. 4,101,457, to Place et al., issued July 18, 1978, and in U.S. Patent No. 4,507,219, to Hughes issued March 26, 1985, whereby all of the above are incorporated herein by reference.

[0035] As to the lipase which may be employed in this invention, such enzymes are well known and commercially available, and are produced, for example, by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19,154, as described in British Patent 1,372,034, the disclosure of which is incorporated herein by reference. Another lipase which may be used is the D96L lipase enzyme derived from *Humicola lanuginosa* as described in U.S. Patent No. 5,929,022, the disclosure of which is incorporated herein by reference.

[0036] Regarding the amylase which may be employed in this invention, such enzymes are well known and commercially available. They include α -amylase obtained from, for example, *B. licheniformis* (from Novo), as well as those sold under the name of Rapidase (by Gist-Brocades) and Termamyl and BAN (by Novo).

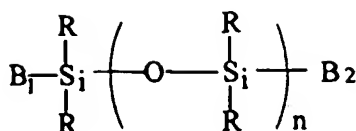
[0037] Still other additives which may optionally be employed in the stain removal composition of this invention include anti-redeposition agents, builders, chelators, fragrances, hydrotropes, enzyme stabilizers, bleaches, fluorescers mixtures thereof and the like, all of which are known compounds and commercially available.

[0038] The anti-redeposition agents which may be used include, for example, cellulosic polymers and salts like sodium sulphate as well as copolymers derived from acrylic acid and lauryl methacrylate, like Narlex DC-1, made available by National Starch and Chemical. Others include polycarboxylic acids such as those sold under the name of Alcosperse 725 and made commercially available by Alco. The builders (sequesters) which may be used include citrates like sodium citrate, and phosphates like sodium tripolyphosphate. The chelators which may be used are those which are well known in the art and they typically include ethylene diamine tetracetic acid as well as nitrilotriacetic acid. The fragrances which may be used in the stain removal compositions of this invention include those conventionally used in cleaning compositions and made commercially available by, for example, Bush Booke Allen, Inc. and Quest International. The hydrotropes which may be used in this invention are known in the art and include sodium xylene sulfonate, sodium cumene sulfonate, ethanol, urea or mixtures thereof. Regarding the enzyme stabilizers which may be used in this invention, such stabilizers are often selected from the group consisting of glycerol sorbitol, berate oxide, borax, alkali metal borates, and preferably, boric acid.

[0039] The bleaches which may be used in this invention include hydrogen peroxide, chlorine dioxide, tetracetylene diamine, mixtures thereof and the like. The fluorescers which may be used in this invention include those generally classified as stilbenes, oxazoles, benzoxazoles, benzimidazoles and the like. Preferred fluorescers are made available under the name of Tinopal (Ciba Geigy) and Optiblanc (3V, Inc.).

[0040] The amount of optional additives employed in the stain removal composition of this invention is limited only to the extent the amount used does not prevent the stain removal composition from minimizing the impact of the forces and interactions between the contaminant targeted for removal and the substrate. Typically, however, the total amount of optional additive used in the stain removal composition of this invention is from about 0.0% to about 15%, and preferably, from about 0.1% to about 12%, and most preferably, from about 1.0% to about 10% by weight, based on total weight of the stain removal composition, including all ranges subsumed therein.

[0041] When preparing the stain removal composition of this invention, there is no limitation with respect to the processing steps as long as the resulting composition is one which may be used in a cleaning application. Essentially, the components (e.g., stain removal surfactant, solvent) of the stain removal composition are, for example, mixed, stirred or agitated using any art recognized technique. The stain removal compositions may be made at ambient temperature, atmospheric pressure or at any pressure or temperature variations which may result in a stain removal composition. The addition of such components is not limited to any particular order, with the proviso that the resulting



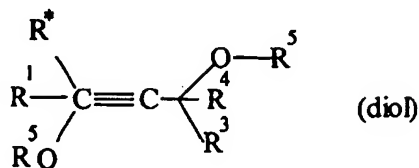
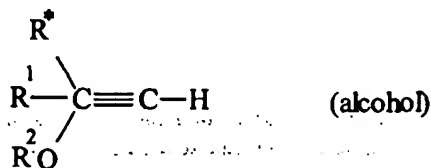
wherein n is an integer from about 1 to about 10,000, preferably from about 1 to about 100.

[0052] At least one and preferably, both of B_1 and B_2 are solvent phobic groups such as lipophilic or hydrophilic (e.g., anionic, cationic) groups, but are not CO_2 -philic groups. Each R is independently an alkyl, aryl or haloalkyl, with perfluoroalkyl, C_1 - C_4 alkyls, phenyl and trifluoropropyl being the preferred R groups.

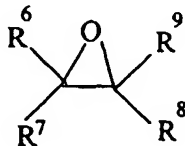
[0053] Regarding B_1 and B_2 , such end-functional groups may be derived from silicones with reactive groups that yield end-functional materials upon contact with a substrate. Illustrative examples of such reactive groups include vinyl, hydride, silanol, alkoxy/polymeric alkoxide, amine, epoxy, carbinol, methacrylate/acrylate, mercapto, acetoxy/chlorine/dimethylamine moieties.

[0054] A more detailed description of the types of end-functionalized polysiloxanes which may be used in this invention may be found in WO 99/10587, the disclosure of which is incorporated herein by reference.

[0055] Other continuous phase surfactants which may be employed in this invention include those generally classified as acetylenic alcohols or diols as represented by the formulae below, respectively:



wherein R^* , R^1 , R^3 and R^4 are each independently hydrogen atoms or linear or branched alkyl groups comprised of 1 to 38 carbons, and R^2 and R^5 are each hydrogen atoms or hydroxyl terminated polyalkylene oxide chains derived from 1 to 30 alkylene oxide monomer units of the following structure:



wherein R^6 , R^7 , R^8 and R^9 are each independently hydrogen atoms, linear or branched alkyl groups having about 1 to about 5 carbons, or phenyl.

[0056] Still other continuous phase surfactants which may be employed in this invention include alkoxyated fatty alcohols having, for example, ethoxy or ethoxy and propoxy in a ratio of about 2:1 and an aliphatic chain comprising from about 8 to about 15 carbon atoms. These types of surfactants are most often preferred when the solvent employed is a biodegradable functionalized hydrocarbon.

[0057] The most preferred and the superior continuous phase surfactants which may be used in this invention

the additive does not interfere with the cleaning process.

[0064] The examples below are provided for illustrative purposes, and they are not intended to restrict the scope of the invention. Thus, various changes may be made to the specific embodiments of this invention without departing from its spirit. Accordingly, the invention is not to be limited to the precise embodiments shown and described, but only as indicated in the following claims.

[0065] Stain removal (extent cleaning) was measured with a Hunter Ultrascan XE Spectrophotometer. The L, a, b scale was used to measure cleaning, and the results are reported as a stain removal index value (SRI) by using the following formula:

$$SRI = 100 - \left(\left(L_{\text{washed}} - L_{\text{clean}} \right)^2 + \left(a_{\text{washed}} - a_{\text{clean}} \right)^2 + \left(b_{\text{washed}} - b_{\text{clean}} \right)^2 \right)^{\frac{1}{2}}$$

wherein

L measures black to white differences;
a measures green to red differences; and
b measures blue to yellow differences.

[0066] Least Significant Difference stain removal index values for all comparisons were calculated using the method described in Statistical Principles of Research Design and Analysis, Duxbury Press, by Robert O. Kuehl, (1994). The values below are based on four (4) observations for each group investigated.

Example 1

[0067] Swatches of cotton cloth, about 22 cm x 13 cm, were inscribed in pencil, with a circle having a diameter of about 5 cm. Six hundred (600) microliters of coffee (prepared by adding about 9 tablespoons of coffee and 2.5 cups of water to an automatic drip coffee maker) were applied inside the circles of the swatches after cooling. The cooled coffee was applied via a micropipet and the resulting stained swatches were dried overnight.

Example 2

[0068] Four swatches (prepared in Example 1) were placed in a cleaning chamber of a dry cleaning unit suitable for cleaning with carbon dioxide. The dry cleaning unit was constructed in the manner described in U.S. Patent No. 5,467,492. The cleaning chamber was also charged with 11 pounds of cotton sheets (about 28 cm²) to simulate a full load of laundry. Carbon dioxide was circulated in the machine at a rate of about 490 liters of liquid CO₂ per cleaning loop, and a storage tank was employed to feed the unit with clean carbon dioxide. The cleaning cycle lasted for about 15 minutes and the carbon dioxide was pressurized to about 850 psi at 11°C. Subsequent to the cleaning cycle, the liquefied CO₂ was circulated back to the storage tank and the swatches were removed. The SRI calculated by averaging the SRI for each of the four (4) swatches was 70.5

Example 3

[0069] The experiment of Example 3 was conducted in a manner similar to the experiment described in Example 2 except that the carbon dioxide solvent was charged with 0.05% (weight/volume) organosilicone surfactant (Monasil PCA, commercially available from Mona Industries) and 0.05% (weight/volume) water. Also, the four (4) swatches in this example were subjected to the stain removal composition of this invention having ethoxylated polyorganosiloxane (Silwet L-7602), (10.0%); ethanol (10.0%); glycerol triacetate (8.0%); N-octylpyrrolidone (2.0%); Narlex DC-1 anti-redeposition polymer (1.0%) and a balance of water, wherein all percents are by weight based on total weight of the stain removal composition. The spray spotter was applied via a trigger spray bottle (i.e., about 4 full and quick pulls of the trigger with the nozzle of the spray bottle being about 8 inches away from each stained swatch.) The SRI calculated by averaging the SRI for each of the 4 swatches was 84.7.

Example 13

[0079] The experiment of Example 13 was conducted in a manner similar to the experiment conducted in Example 2 except that the swatches were stained with shoe polish in lieu of coffee. The SRI calculated by averaging the SRI for each of the 4 swatches was 74.9.

Example 14

[0080] The experiment of Example 14 was conducted in a manner similar to the one described in Example 8 except that the swatches were cotton and the stain removal composition consisted of 90% by weight water and 10% by weight Silwet L-7602. The SRI calculated by averaging the SRI of the 4 swatches was 70.9

Example 15

[0081] The experiment of Example 15 was conducted in a manner similar to the one described in Example 14 except that no stain removal composition was used. The SRI calculated by averaging the SRI of the 4 swatches was 59.3.

Example 16

[0082] The experiment of Example 16 was conducted in a manner similar to the one described in Example 2 except that the cow blood was used in lieu of coffee. The SRI calculated by averaging the SRI of the 4 swatches was 58.9

Example 17

[0083] The experiment of Example 17 was conducted in a manner similar to the one described in Example 3 except that the stain removal composition comprised Silwet L-77 (1.0%); Neodol 25-9 (10.0%); propylene glycol (1.0%); Alcosperse 725 (1.0%) and a balance of water. Also, in lieu of Monasil.PCA, 0.128% (w/v) of a detergent consisting of Silwet L-7602, water and propylene glycol (40%, 40%, 20% by weight, respectively) was used, and commercially available swatches (e.g., from Kraefeld of Germany) stained with coffee; blood or red wine were used. The data in Table I depicts the % stain removal obtained when using the stain removal composition of Example 17.

TABLE I% Soil Removal

Swatch stain	A	B	C
Coffee	-0.4	-4.0	7.0
Blood	3.5	3.6	15.2
Red Wine	-0.1	-0.2	8.5

A = pure Carbon Dioxide

B = as described in Example 17, except no stain removal composition used

C = as described in Example 17

and pressure, a biodegradable functionalized hydrocarbon or a silicone comprising solvent;

b) optionally, a polar fluid;

c) a substrate treated with a stain removal composition comprising at least one stain removal surfactant, the stain removal surfactant being a nonionic, anionic, cationic, amphoteric or zwitterionic compound or mixture thereof; and

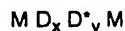
d) optionally, a continuous phase surfactant, the continuous phase surfactant capable of forming a reverse micelle in a continuous phase formed by the solvent.

8. A dry cleaning composition according to claim 7 wherein the solvent that is a gas at standard temperature and pressure is a C₂-C₄ substituted or unsubstituted alkane or carbon dioxide, the solvent that is a biodegradable functionalized hydrocarbon is an azeotropic solvent, and the solvent that is a silicone comprising solvent is a cyclic siloxane.

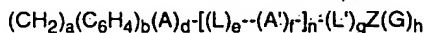
9. A dry cleaning composition according to claim 7 wherein the polar fluid is water.

10. A dry cleaning composition according to claim 7 wherein the stain removal surfactant is selected from the group consisting of an organosiloxane, an alkoxylate, N-octylpyrrolidone, sodium diethylhexyl sulfosuccinate, sodium methyl benzene sulfonate or mixtures thereof.

11. A dry cleaning composition according to claim 7 wherein the continuous phase surfactant is aerosol OT, didodecyl dimethylammonium bromide, polyoxyethylene ether, lecithin, end-functionalized polysiloxane, an acetylenic alcohol, a acetylenic diol, an alkoxylated fatty alcohol, or a siloxane having the formula:



wherein M is a trialkylsiloxyl end group, D_x is a dialkylsiloxyl backbone which is solvent-philic and D^{*}_y is one or more alkylsiloxyl groups which are substituted with a solvent-phobic group wherein each solvent phobic group is independently defined by the formula:



wherein a is 1-30,

b is 0 or 1,

C₆H₄ is unsubstituted or substituted with a C₁₋₁₀ alkyl or alkenyl, and A and A' are each independently a linking moiety representing an ester, a keto, an ether, a thio, an amido, an amino, a C₁₋₄ fluoroalkyl, a C₁₋₄ fluoroalkenyl, a branched or straight chained polyalkylene oxide, a phosphate, a sulfonyl, a sulfate, an ammonium, and mixtures thereof,

L and L' are each independently a C₁₋₃₀ straight chained or branched alkyl or alkenyl or an aryl which is unsubstituted or substituted,

E is 0-3,

F is 0 or 1,

N is 0-10,

G is 0-3,

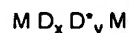
O is 0-5,

Z is a hydrogen, carboxylic acid, a hydroxy, a phosphato, a phosphate ester, a sulfonyl, a sulfonate, a sulfate, a branched or straight-chained polyalkylene oxide, a nitril, a glyceryl, an aryl unsubstituted or substituted with a C₁₋₃₀ alkyl or alkenyl, a carbohydrate unsubstituted or substituted with a C₁₋₁₀ alkyl or alkenyl or an ammonium,

G is an anion or cation such as H⁺, Na⁺, Li⁺, K⁺, NH₄⁺, Ca⁺², Mg⁺², Cl⁻, Br⁻, I⁻, mesylate, or tosylate, and

h is 0-3.

12. A dry cleaning composition according to claim 1 wherein the composition does comprise carbon dioxide as the solvent, water as the polar fluid, a stain removal surfactant comprising an organosiloxane, alkoxylate, N-octylpyrrolidone, sodium diethyl hexyl sulfosuccinate, sodium methyl benzene sulfonate or mixtures thereof, and a continuous phase surfactant having the formula:



wherein M is a trialkylsiloxyl end group, D_x is a dialkylsiloxyl backbone which is solvent-philic and D^{*}_y is one or more

O is 0-5,

Z is a hydrogen, carboxylic acid, a hydroxy, a phosphato, a phosphate ester, a sulfonyl, a sulfonate, a sulfate, a branched or straight-chained polyalkylene oxide, a nitril, a glyceryl, an aryl unsubstituted or substituted with a C₁₋₃₀ alkyl or alkenyl, a carbohydrate unsubstituted or substituted with a C₁₋₁₀ alkyl or alkenyl or an ammonium,

G is an anion or cation such as H⁺, Na⁺, Li⁺, K⁺, NH₄⁺, Ca⁺², Mg⁺², Cl⁻, Br⁻, I⁻, mesylate, or tosylate, and h is 0-3.

16. A process according to claim 13 wherein the solvent is carbon dioxide.

17. A process according to claim 13 wherein the stain removal composition comprises a stain removal surfactant selected from the group consisting of an organosiloxane, an alkoxylate, N-octylpyrrolidone, sodium diethylhexyl sulfosuccinate, sodium methyl benzene sulfonate or mixtures thereof.

18. A process according to claim 13 wherein the substrate is clothing.

19. A substrate having been subjected to:

(a) a stain removal composition; and

(b) a solvent which is a gas at standard temperature and pressure, a biodegradable functionalized hydrocarbon or a silicon comprising solvent.

20. A substrate according to claim 19 wherein the substrate is clothing.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 00 20 3256

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (In.CI.7)
Y	GB 2 335 662 A (RAJAN MUSTAQ ALI) 29 September 1999 (1999-09-29) * the whole document *	1-20	
			TECHNICAL FIELDS SEARCHED (In.CI.7)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 18 January 2001	Examiner Saunders, T
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**ANNEX TO THE EUROPEAN SEARCH REPORT
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EP 00 20 3256

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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